09/787310
JC0[illegible]c'd PCT/PTO 1 4 MAR 2001

~~Process for producing formed cellulosic articles~~

Ins. B[1]

The invention relates to a process for producing formed cellulosic articles, such as fibres, filaments, sheetings, membranes or tubes, comprising a) extruding a solution of cellulose in an aqueous amine oxide, particularly N-methylmorpholine N-oxide, through an extrusion die via an air gap and coagulating the formed article in an aqueous precipitation bath containing amine oxide, and b) passing the formed article through at least one washing stage for removing residual amine oxide.

While the precipitation bath usually has concentrations of N-methylmorpholine N-oxide (NMMO) from 10 to 25 % by mass and temperatures from 0 to 20°C, in the subsequent washing stages the NMMO content of the washing liquors is decreased to nearly 0 % at temperatures up to 80°C. It is known that these NMMO-containing liquors are characterized by a partially very strong growth of microorganisms. These biological substances are sustantially bacteria and fungi and cause considerable difficulties with the processing by the formation of slime aggregates and biofilms. The function of parts of the production plant can be impaired by clogging of pipes, filters, pumps etc. up to their total breakdown. A mechanical cleaning of the washing and precipitation bath systems is very expensive due to the marked adhesion of the polymeric slime substances to all the surfaces and results in unwanted interruptions of the production process.

From WO 96/18761 a process is known in which the biological substances in the baths are degraded by using usual oxidants, such as e.g. hydrogen peroxide, peracetic acid, ozone or chlorine

dioxide. With this method it must be assured by an expensive mechanism that these oxidants are completely disposed before recycling the NMMO into the dope production stage.

According to the process specified in WO 97/07137 a microbicidal agent is added during or after the regeneration of solutions containing amine oxide in order to avoid formation of films in the apparatus. In this case likewise the disadvantage exists that the added substance or its degradation products are concentrated in the NMMO cycle of the process and cause unwanted effects in the individual process steps. The consequences for the thermal stability of the NMMO and the accompanied safety risk must be particularly critically considered.

From WO 97/07108 and WO 97/07138 the UV treatment of amine oxide containing solutions is known with the aim to destroy the N-nitrosomorpholine formed during or after the oxidation of N-methylmorpholine (NMM) to NMMO. The UV treatment is restricted to the regeneration of the precipitation bath for the purpose of reusing the regenerated NMMO for preparing the dope.

It is the object of the invention to avoid the formation and growth of the coatings, films and slime aggregates formed by microorganisms in the parts of the plant having contact with the NMMO containing liquors and the impairment and operating troubles caused thereby. Particularly the above-mentioned process should not require frequent cleaning of the plant even in a continuous operation. Furthermore, it should be refrained from using chemical substances in order to avoid the problems of their monitoring and, if required, their re-separation accompanied therewith. Further advantages can be gathered from the following specification.

With the process specified at the beginning, according to the invention these objects are achieved in that the liquor of the precipitation bath in the precipitation stage and/or the washing liquor of the washing stage(s) is treated by ultra-violet radiation. Surprisingly it has been found that the microorganisms developing in liquors containing amine oxide, particularly NMMO, which microorganisms result in the unwanted deposits, are deactivated by the UV radiation or their DNS (deoxyribonucleic acid) is killed by a UV induced reaction. As a result the total germ number in the liquor is maintained low, and possible cleanings of the plant are only necessary after substantially longer operating periods.

According to the preferred embodiment of the process of the invention a ultra-violet radiation of a wave length in the range from 200 to 280 nm is used. Especially the used UV radiation has a wave length of 254 nm. Conveniently this radiation is generated by a mercury low-pressure lamp the maximum intensity of which is at this wave length.

Preferably the UV treatment of the liquors of the washing stage(s) is limited to a temperature below 50°C. When operating with several washing steps in series the temperature of the washing liquor of the last steps is often elevated above 50°C in order to support washing the amine oxide out of the formed articles. In these stages the UV radiation treatment can be omitted because the microorganisms cannot develop at these temperatures. On the other hand the growth of the microorganisms is strongly inhibited at temperatures below 20°C. As the precipitation baths are frequently maintained below this temperature the radiation can then be markedly reduced. As far as it is possible in the subsequent washing stages to avoid temperatures between 20 and 40°C, the radiation power can be reduced also in those stages.

Preferably the precipitation bath liquors or the washing liquors having a Hazen Color Number Hz $\leq$ 400 are subjected to the UV treatment. It has been found that more intense colorings of the liquors reduce the efficiency of the UV treatment and require higher radiation powers. The effectivity of the UV treatment is ensured up to said Hazen Color Number. Consequently, suppressing the formation of colored side products is also advantageous with the UV treatment of the precipitation bath and washing liquors according to the invention aside from other reasons.

If with the process of the invention the precipitation bath and several washing stages are connected in series and comprise liquor cycles of their own, the cycle liquors of the precipitation bath and the first washing stage(s) are treated with UV radiation because these liquors offer comparatively favorable conditions (temperature, content of organic substances) for the development of microorganisms. As the liquor from the last washing stage is passed to the precipitation bath opposite to the movement of the fibres, it is repeatedly exposed to the UV radiation on this path. The UV radiation in a cycle can be carried out continuously or intermittently. It is possible to integrate the UV radiators in a simple manner also in already existing plants.

Preferably the cycle liquors are irradiated with a power in the range from 0.1 to 1.0 Wh/l, especially with 0.5 Wh/l. The conditions for the microbiological growth and the effectiveness of its combat by UV radiation are very different depending on the pH value, temperature, concentration of NMMO, oxygen introduction and light transmission (color number). The respective specific conditions can be taken into account by adapting the power and duration of the UV irradiation.

The figure shows a diagrammatic representation of a plant for carrying out the process of the invention with a precipitation

bath and a connected five-stage washing part.

The precipitation bath has an internal cycle for the bath liquor from the catch vat 1^b to the spinning vessel 1^a with a pump 1^c, a cooler 1^d and a UV radiator 1^e. Spent precipitation bath is withdrawn via line 1^f and passed to a cleaning stage 2. The cleaned precipitation bath is concentrated in the stage 3. The formed NMMO concentrate is used in the stage 4 for preparing the dope which is pumped to the spinnerets. The distillate formed in the stage 3 is fed as washing liquor to the last washing stage 9.

The first washing stage 5 has an external washing liquor cycle 5^a with an UV radiator 5^e. NMMO-containing washing liquor is passed from the cycle 5^a via a line 5^b to the catch vat 1^b. The second washing stage 6 is provided with an UV radiator 6^e in the same manner as the first washing stage 5. The further washing stages 7,8 and 9 have likewise external washing agent cycles 7^a, 8^a and 9^a, respectively, which differ from the cycles 5^a and 6^a in that no UV radiator is arranged in them because the temperatures of the washing agent is here maintained above 50°C. The path of the extruded products through the plant is shown by a dashed line.

Practical Example

In the plant shown in the figure the UV radiators are operated with a power of 0.5 Wh/l circulated liquor. The total germ number was determined in intervals of 2 days with samples from the precipitation bath by means of cultures (TTC Agar). The total germ number was continuously below 10^5/ml. A cleaning was only necessary after 2 months.

Comparative Example

With the same procedure as in the practical example, however without the UV irradiation, an increase of the total germ number

to $> 10^6$/ml was already found after 5 days inspite of a careful cleaning and disinfection.